

[Document] SPECIFICATION

[Title of the Invention] NONAQUEOUS ELECTROLYTE  
SECONDARY BATTERY

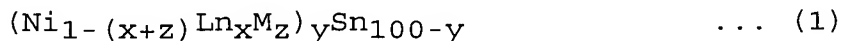
[What is claimed is:]

[Claim 1] A nonaqueous electrolyte secondary battery characterized by comprising: a positive electrode; a negative electrode containing an alloy having a TiNiSi type crystal structure; and a nonaqueous electrolyte.

[Claim 2] The nonaqueous electrolyte secondary battery according to claim 1, characterized in that a lattice constant of crystal axis b of the TiNiSi type crystal structure falls within a range of 4Å to 5.5Å.

[Claim 3] The nonaqueous electrolyte secondary battery according to claim 1 or 2, characterized in that the alloy contains Sn.

[Claim 4] The nonaqueous electrolyte secondary battery according to any one of claims 1 to 3, characterized in that the alloy has a composition represented by formula (1) given below:



where Ln denotes at least one kind of element selected from the elements having an atomic radius falling within a range of  $1.6 \times 10^{-10}$  m to  $2.2 \times 10^{-10}$  m, M is at least one element selected from the group consisting of Ti, V, Co, Fe and Nb, and x, y and z satisfy the conditions of  $0.4 \leq x + z \leq 0.7$ ,  $40 \leq y \leq 80$  and  $0 \leq z \leq 0.2$ .

[Claim 5] A nonaqueous electrolyte secondary battery characterized by comprising: a positive electrode; a negative electrode containing an alloy having a ZrBeSi type crystal

structure; and a nonaqueous electrolyte.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a nonaqueous electrolyte secondary battery.

[0002]

[Prior Art]

In recent years, a nonaqueous electrolyte battery using lithium as the negative electrode active material attracts attention as a high energy density battery, and a primary battery using, for example, manganese dioxide ( $\text{MnO}_2$ ), carbon fluoride  $[(\text{CF}_2)_n]$ , or thionyl chloride ( $\text{SOCl}_2$ ) as the positive electrode active material is already in wide use as a power source for desk-top calculators, watches, and as memory back-up batteries. Further, with progress achieved in recent years in miniaturization and weight reduction in various electronic appliances such as VTRs and communication appliances, the demands have been increased for a secondary battery having a high energy density for use as the power source for such appliances. Much research is thus being conducted on a lithium secondary battery using lithium as the negative electrode active material.

[0003]

Specifically, research is being conducted on a lithium secondary battery comprising a negative electrode containing metal lithium, and a positive electrode containing as a positive electrode active material which is a compound (e.g.,

TiS<sub>2</sub>, MoS<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, V<sub>6</sub>O<sub>13</sub>, and MnO<sub>2</sub>) capable of carrying out a topochemical reaction with lithium and a lithium conductive solid electrolyte or a nonaqueous electrolysis solution prepared by dissolving a lithium salt such as LiClO<sub>4</sub>, LiBF<sub>4</sub> or LiAsF<sub>6</sub> in a nonaqueous solvent such as propylene carbonate (PC), 1,2-dimethoxy ethane (DME),  $\gamma$ -butyrolactone ( $\gamma$ -BL) or tetrahydrofuran (THF).

[0004]

However, the lithium secondary battery outlined above has not yet been put into practical use. It should be noted in this connection that lithium used in the negative electrode is pulverized after the secondary battery is repeatedly subjected to the charge-discharge operation. As a result, the lithium is converted into a highly-reactive lithium dendrite, which impairs the safety of the secondary battery. Also, related damage, short-circuiting and thermal runaway of the battery tend to be brought about. In addition, the charge-discharge efficiency is lowered, which shortens the cycle life.

[0005]

Under the circumstances, it is proposed to use a carbonaceous material capable of absorbing-desorbing lithium, such as coke, a baked resin, a carbon fiber or a vapor-grown carbon in place of the metal lithium. The lithium ion secondary battery that has been commercialized in recent years comprises a negative electrode containing a carbonaceous material, a positive electrode containing LiCoO<sub>2</sub>, and a nonaqueous electrolyte. In this lithium ion secondary battery, a further improvement in the charge-discharge capacity

per unit volume is required in accordance with the demands for the further miniaturization of electronic appliances and for the continuous use of the secondary battery over a longer period of time. Such being the situation, vigorous research is being conducted in an attempt to develop a lithium ion secondary battery meeting these requirements. However, a sufficiently satisfactory result has not yet been obtained. Therefore, it is necessary to develop a new negative electrode material for commercializing a secondary battery having a larger capacity.

[0006]

It is proposed to use an elemental metal such as aluminum (Al), silicon (Si), germanium (Ge), tin (Sn), or antimony (Sb) as a negative electrode material that permits obtaining a capacity larger than that obtained by a carbonaceous material. Particularly, in the case of using Si as a negative electrode material, it is possible to obtain a large capacity, i.e., a capacity of 4,200 mAh per unit weight (1g). However, in the case of using a negative electrode formed of the elemental metal exemplified above, the bond between the adjacent metal atoms is broken due to the repetition of the absorption-desorption of Li, which leads to fine pulverization of the negative electrode, resulting in failure to obtain high charge-discharge cycle characteristics.

[0007]

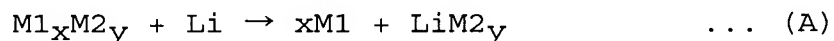
Under the circumstances, it is attempted to improve the charge-discharge cycle life of the secondary battery by using as the negative electrode material an alloy containing element

M1 (e.g., Ni, V, Ti or Cr) that does not form an alloy with lithium, and element M2 forming an alloy with lithium. Also, in order to suppress the pulverization of the negative electrode material, which causes the deterioration of the cycle characteristics of the secondary battery, it is attempted to suppress the volume expansion by dispersing, for example, a phase reactive with lithium (e.g., an element M2 phase), and a phase that is inactive with lithium (e.g., an element M1 phase) in a nano scale, or by making the entire alloy phase amorphous.

[0008]

In any of the negative electrode materials described above, an alloying reaction is carried out between the negative electrode material and lithium so as to permit lithium to be absorbed by the negative electrode material. The initial charging reaction is as exemplified by reaction formula (A) given below:

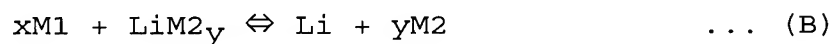
[0009]



The second charge-discharge reaction et seq. after the initial charge-discharge reaction proceeds as denoted by reaction formula (B) of chemical formula 1 given below:

[0010]

[Chemical formula 1]



[0011]

Since the reaction in the second reaction et seq. given by reaction formula (B) does not proceed completely reversibly,

Li is retained inside the alloy, and the lithium supply source is depleted if the charge-discharge cycle is repeated, which makes it impossible to further repeat the charge-discharge cycle. Incidentally, in the case of an amorphous alloy, the reaction proceeds smoothly in the initial stage. However, the crystallization of the amorphous alloy is promoted if the charge-discharge cycle is repeatedly carried out, with the result that the cycle deterioration is generated at the stage where the crystallization is promoted.

[0012]

It should also be noted that the negative electrode material that carries out an alloying reaction with lithium in the charging stage exhibits a high reactivity with the nonaqueous electrolyte containing a nonaqueous solvent such as ethylene carbonate and, thus, a film of, for example,  $\text{Li}_2\text{CO}_3$ , is formed on the surface of the negative electrode as a result of the reaction carried out between lithium contained in the negative electrode material and the nonaqueous electrolyte. It follows that the Coulomb efficiency is lowered during the charge-discharge cycle. Further, in the case of using a positive electrode active material such as  $\text{LiCoO}_2$  as a lithium supply source, lithium in the supply source is depleted with progress in the charge-discharge cycle, with the result that a clear capacity deterioration is observed.

[0013]

A nonaqueous electrolyte secondary battery comprising a negative electrode containing an alloy formed of at least two kinds of elements, the alloy having a hexagonal close-packed

structure and a  $\text{Ni}_2\text{In}$  type structure, is disclosed in Jpn. Pat. Appln. KOKAI Publication No. 2001-250541 (Patent Document 1). In this negative electrode, an element  $\text{M}^1$  such as tin or aluminum, which is capable of electrochemically carrying out an alloying reaction with lithium, is alloyed with lithium so as to charge the secondary battery (described in paragraph [0009]). Therefore, lithium is stored within the alloy with progress in the charge-discharge cycle so as to decrease the lithium amount contributing to the charge-discharge operation. In addition, this negative electrode has a high reactivity with the nonaqueous electrolyte and, thus, the Coulomb efficiency is low during the charge-discharge cycle. It follows that the secondary battery disclosed in patent document 1 is incapable of obtaining a long charge-discharge cycle life.

[0014]

[Patent document 1]

Jpn. Pat. Appln. KOKAI Publication No. 2001-250541 ([What is claimed is:], paragraphs [0009] and [0013] - [0015])

[0015]

[Object of the Invention]

An object of the present invention is to provide a nonaqueous electrolyte secondary battery excellent in both the charge-discharge cycle life and the discharge capacity per unit volume.

[0016]

[Means for Achieving the Object]

A first nonaqueous electrolyte secondary battery according to the present invention comprises: a positive

electrode; a negative electrode containing an alloy having a TiNiSi type crystal structure; and a nonaqueous electrolyte.

[0017]

A second nonaqueous electrolyte secondary battery according to the present invention comprises: a positive electrode; a negative electrode containing an alloy having a ZrBeSi type crystal structure; and a nonaqueous electrolyte.

[0018]

[Embodiments of the Invention]

A first nonaqueous electrolyte secondary battery according to an embodiment of the present invention will now be described. The nonaqueous electrolyte secondary battery comprises a positive electrode, a negative electrode containing an alloy having a TiNiSi type crystal structure, and a nonaqueous electrolyte layer provided between the positive electrode and the negative electrode.

[0019]

The negative electrode, the positive electrode and the nonaqueous electrolyte layer will now be described.

[0020]

#### 1) Negative Electrode

FIG. 1 schematically shows the construction of the unit cell of the TiNiSi type crystal, covering the case where the alloy has an LaNiSn composition. Specifically, the circles shaded with oblique lines denote La sites, the white circles denote Ni sites, and the circles shaded with dots denote Sn sites.



[0021]

It is possible for the alloy to be a single phase alloy consisting of a TiNiSi type crystal phase or to be a polyphase alloy including a TiNiSi type crystal phase and another crystal phase.

[0022]

The crystal axis b of the TiNiSi type crystal is the crystal axis parallel to the depth direction in FIG. 1. Lithium is inserted into the free space between the adjacent layers in a direction perpendicular to crystal axis b. It is desirable for the lattice constant of crystal axis b to fall within a range of 4Å to 5.5Å. That is because, if the lattice constant of crystal axis b is smaller than 4Å, it is difficult to interpose the lithium ions between the adjacent layers of the crystal, and on the other hand, if the lattice constant of crystal axis b exceeds 5.5Å, the TiNiSi type crystal phase possibly fails to be obtained. It is preferable for the lattice constant of crystal axis b to fall within a range of 4.2Å to 5.3Å.

[0023]

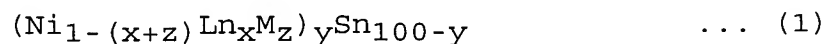
It is desirable for the elements constituting the alloy to include Sn because this will enable the secondary battery to exhibit a higher discharge capacity per unit volume. It is more desirable for the elements constituting the alloy to include at least one kind of element, Ln, selected from the elements having an atomic radius falling within a range of  $1.6 \times 10^{-10}$  m to  $2.2 \times 10^{-10}$  m, in addition to Sn, which makes it possible for the absorbing-desorbing reaction of lithium to

be carried out more smoothly. It is also possible to increase the stability of the crystal so as to permit the lattice constant of crystal axis  $b$  to fall within a range of  $4\text{\AA}$  to  $5.5\text{\AA}$ .

[0024]

The composition of the alloy is not particularly limited as long as the alloy includes the TiNiSi type crystal phase. However, it is desirable for the alloy to have a composition represented by formula (1) given below:

[0025]



where Ln denotes at least one kind of element selected from the elements having an atomic radius falling within a range of  $1.6 \times 10^{-10}$  m to  $2.2 \times 10^{-10}$  m, M is at least one element selected from the group consisting of Ti, V, Co, Fe and Nb, and  $x$ ,  $y$  and  $z$  satisfy the conditions of  $0.4 \leq x + z \leq 0.7$ ,  $40 \leq y \leq 80$  and  $0 \leq z \leq 0.2$ .

[0026]

The alloy used in the present invention contains at least one kind of element Ln selected from the elements having an atomic radius falling within a range of  $1.6 \times 10^{-10}$  m to  $2.2 \times 10^{-10}$  m. Use of Ln permits the lithium ions to be interposed easily between the adjacent layers of the crystal. In the case of using an element having an atomic radius, which exceeds  $2.2 \times 10^{-10}$  m or which is smaller than  $1.6 \times 10^{-10}$  m, as element Ln, it is difficult to maintain the TiNiSi type crystal structure or it is difficult to interpose the lithium ions between the adjacent layers of the crystal.

[0027]

The elements Ln that can be used desirably include, for example, La (an atomic radius of  $1.88 \times 10^{-10}$  m), Ce (an atomic radius of  $1.83 \times 10^{-10}$  m), Pr (an atomic radius of  $1.83 \times 10^{-10}$  m), Nd (an atomic radius of  $1.82 \times 10^{-10}$  m), Pm (an atomic radius of  $1.80 \times 10^{-10}$  m), Sm (an atomic radius of  $1.79 \times 10^{-10}$  m), Mg (an atomic radius of  $1.60 \times 10^{-10}$  m), Ca (an atomic radius of  $1.97 \times 10^{-10}$  m), Sr (an atomic radius of  $2.15 \times 10^{-10}$  m), Ba (an atomic radius of  $2.18 \times 10^{-10}$  m), Y (an atomic radius of  $1.82 \times 10^{-10}$  m), Zr (an atomic radius of  $1.62 \times 10^{-10}$  m), and Hf (an atomic radius of  $1.60 \times 10^{-10}$  m).

[0028]

If the sum atomic ratio ( $x + z$ ) of the element Ln and the element M is smaller than 0.4, it is difficult to interpose the lithium ions between the adjacent layers of the crystal, possibly resulting in failure to obtain a high charging capacity. On the other hand, if the sum atomic ratio ( $x + z$ ) exceeds 0.7, a phase (e.g., a LnSn phase), which performs easily an alloying reaction in a large amount with lithium, is formed in addition to the TiNiSi type crystal structure, with the result that the charge-discharge cycle life of the secondary battery tends to be shortened. It is more desirable for the sum atomic ratio ( $x + z$ ) to fall within a range of 0.45 to 0.65.

[0029]

It is also possible to permit at least one kind of element, M, selected from the group consisting of Ti, V, Co, Fe and Nb to be contained in the alloy. Where the alloy contains

at least one kind of element M, it is possible to stabilize the crystal structure and to prolong the charge-discharge cycle life of the secondary battery. It should be noted, however, that, if the addition amount  $z$  of element M exceeds 0.2, it is difficult to maintain the crystal structure, which may cause a reduction in the charge-discharge capacity or the charge-discharge cycle life. It is more desirable for the addition amount  $z$  of the element M to fall within a range of 0 to 0.15.

[0030]

The reason why the sum atomic ratio  $y$ , i.e., the atomic ratio of the sum of Ni, the element Ln and the element M, is defined to fall within a range of 40 to 80, is that if the sum atomic ratio  $y$  noted above is smaller than 40, the Sn single phase is precipitated, with the result that the pulverization of the alloy tends to be promoted, which shortens the charge-discharge cycle life of the secondary battery, and on the other hand, if the sum atomic ratio  $y$  exceeds 80, the alloy fails to have the TiNiSi type crystal structure such that, for example, the  $\text{Ni}_3\text{Sn}_2$  phase that is quite inactive to lithium constitutes the principal phase of the crystal. It follows that the charge-discharge cycle characteristics or the charge-discharge capacity of the secondary battery would be lowered. It is more desirable for the sum atomic ratio  $y$  to fall within a range of 45 to 75.

[0031]

In the alloy having the TiNiSi type crystal structure, it is possible for a part of the constituting elements to be replaced by another element in order to impart a local strain

to the crystal structure or change the Fermi level of alloy.

[0032]

An alloy having the TiNiSi type crystal structure can be manufactured by, for example, a rapid solidification method. In the rapid solidification method, the raw alloy materials weighed in advance are melted within a crucible in an inert gas atmosphere, followed by spraying the resultant alloy melt onto a cooled body rotated at a high speed so as to obtain a flake-like sample having a thickness of 10 to 50  $\mu\text{m}$ . It is possible to apply a heat treatment to the obtained sample so as to homogenize the texture and the composition of the sample.

[0033]

The negative electrode is prepared by dispersing in a suitable solvent a negative electrode mixture including a negative electrode active material containing an alloy having, for example, the TiNiSi type crystal structure, an electrically conductive agent, and a binder so as to obtain a dispersion, followed by coating one surface or both surfaces of a current collector with the resultant suspension and subsequently drying the coating.

[0034]

Also, as the negative electrode active material, adding a carbonaceous material having a high absorption capability of an alkali metal to the above described alloy for obtaining a mixture improves the absorption capability of the alkali metal such as lithium. It is desirable to use a graphitized material, e.g., a mesophase pitch carbon fiber (MCF), as the carbonaceous material used for preparing the negative electrode

active material.

[0035]

Further, a carbonaceous material is normally used as the electrically conductive agent contained in the negative electrode. If a carbonaceous material having a high absorption capability of the alkali metal and a high electrical conductivity is used as the carbonaceous material contained in the negative electrode, it is possible for the carbonaceous material used as the negative electrode active material to act also as the electrically conductive agent. If graphitized material, which has a high alkali metal absorption capability, such as mesophase pitch carbon fiber, is used singly, the electrical conductivity tends to be lowered. Such being the situation, it is desirable to use a carbon material such as acetylene black or carbon black as an electrically conductive agent together with the graphitized material noted above.

[0036]

The binder used in the present invention includes, for example, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), a fluorinated rubber, a styrene-butadiene rubber (SBR), and carboxy methyl cellulose (CMC).

[0037]

Concerning the mixing ratio of the negative electrode active material, the electrically conductive agent and the binder, it is desirable for the negative electrode active material to be mixed in an amount of 70 to 95% by weight, for the conductive agent to be mixed in an amount of 0 to 25% by weight, and for the binder to be mixed in an amount of 2 to 10%

by weight.

[0038]

The current collector used for the negative electrode is not particularly limited as long as the current collector is formed of an electrically conductive material. For example, it is possible to use a foil, a mesh, a punched metal or a lath metal made of copper, stainless steel or nickel.

[0039]

## 2) Positive Electrode

The positive electrode includes a current collector and a positive electrode active material layer formed on one surface or both surfaces of the current collector.

[0040]

The positive electrode can be prepared by, for example, dispersing in a suitable solvent a positive electrode active material, an electrically conductive agent, and a binder so as to obtain a suspension, followed by coating the surface of the current collector with the resultant suspension and subsequently drying the coating and pressing the dried coating.

[0041]

The positive electrode active material used in the present invention is not particularly limited as long as the substance is capable of absorbing the alkali metal in the discharging stage of the secondary battery and desorbing the absorbed alkali metal in the charging stage of the secondary battery.

[0042]

To be more specific, the positive electrode active

material can be provided by various oxides and sulfides including, for example, manganese dioxide ( $\text{MnO}_2$ ), lithium manganese-containing complex oxides (e.g.,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMnO}_2$ ), lithium nickel-containing complex oxides (e.g.,  $\text{LiNiO}_2$ ), lithium cobalt-containing complex oxides (e.g.,  $\text{LiCoO}_2$ ), lithium nickel cobalt-containing complex oxides (e.g.,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ), lithium manganese cobalt-containing complex oxides (e.g.,  $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ ), and vanadium oxides (e.g.,  $\text{V}_2\text{O}_5$ ). It is also possible for the positive electrode active material to be provided by an organic material such as an electrically conductive polymer material or a disulfide series polymer material.

[0043]

It is more desirable for the positive electrode active material to be provided by a material that permits increasing the battery voltage, such as a lithium manganese-containing complex oxide, (e.g.,  $\text{LiMn}_2\text{O}_4$ ), a lithium nickel-containing complex oxide, (e.g.,  $\text{LiNiO}_2$ ), a lithium cobalt-containing complex oxide, (e.g.,  $\text{LiCoO}_2$ ), a lithium nickel cobalt-containing complex oxide, (e.g.,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ), and a lithium manganese cobalt-containing complex oxide (e.g.,  $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ ).

[0044]

The current collector used in the present invention is not particularly limited as long as the current collector is formed of an electrically conductive material. Particularly, it is desirable for the current collector included in the positive electrode to be formed of a material that is unlikely to be oxidized during the battery reaction. For example, it is



desirable to use aluminum, stainless steel or titanium.

[0045]

The electrically conductive agent used in the present invention includes, for example, an acetylene black, a carbon black and graphite.

[0046]

The binder used in the present invention includes, for example, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF) and a fluorinated rubber.

[0047]

Regarding the mixing ratio of the positive electrode active material, the electrically conductive agent and the binder, it is desirable for the positive electrode active material to be mixed in an amount of 80 to 95% by weight, for the conductive agent to be mixed in an amount of 3 to 20% by weight, and for the binder to be mixed in an amount of 2 to 7% by weight.

[0048]

### 3) Nonaqueous electrolyte layer

The nonaqueous electrolyte layer serves to impart an ionic conductivity between the negative electrode and the positive electrode.

[0049]

It is possible to use a nonaqueous electrolyte layer prepared by allowing a nonaqueous electrolyte solution, which is prepared by dissolving an electrolyte in a nonaqueous solvent, to be supported by a separator formed of a porous material.

[0050]

The separator serves to hold the nonaqueous electrolysis solution and to achieve an electrical insulation between the positive electrode and the negative electrode. The separator used in the present invention is not particularly limited as long as the separator is formed of an insulating material and permits the ion migration between the positive electrode and the negative electrode. For example, it is possible to use a synthetic resin unwoven fabric, a polyethylene porous film or a polypropylene porous film for forming the separator.

[0051]

The nonaqueous solvent used in the present invention includes, for example, a nonaqueous solvent containing as a main component a cyclic carbonate such as ethylene carbonate (EC) or propylene carbonate (PC) and another nonaqueous solvent consisting mainly of a mixed solvent containing a cyclic carbonate and a nonaqueous solvent having a viscosity lower than that of the cyclic carbonate.

[0052]

The nonaqueous solvent having a low viscosity noted above includes, for example, a linear carbonate (for example, dimethyl carbonate, methyl ethyl carbonate, and diethyl carbonate),  $\gamma$ -butyrolactone, acetonitrile, methyl propionate, ethyl propionate, a cyclic ether (for example, tetrahydrofuran and 2-methyl tetrahydrofuran), and a linear ether (for example, dimethoxy ethane and diethoxy ethane).

[0053]

The electrolyte used in the present invention includes,

for example, lithium hexafluoro phosphate ( $\text{LiPF}_6$ ), lithium tetrafluoro borate ( $\text{LiBF}_4$ ), lithium hexafluoro arsenate ( $\text{LiAsF}_6$ ), lithium perchlorate ( $\text{LiClO}_4$ ), and lithium trifluoro metasulfonate ( $\text{LiCF}_3\text{SO}_3$ ). Particularly, it is desirable to use at least one electrolyte of lithium hexafluoro phosphate ( $\text{LiPF}_6$ ) and lithium tetrafluoro borate ( $\text{LiBF}_4$ ).

[0054]

It is desirable for the electrolyte to be dissolved in the nonaqueous solvent in an amount of 0.5 to 2 mol/L.

[0055]

It is possible to use a gel-like material, which is prepared by allowing a polymer material to contain a nonaqueous electrolysis solution, in the nonaqueous electrolyte layer. To be more specific, it is possible to arrange an electrolyte layer formed of the gel-like material between the positive electrode and the negative electrode. It is also possible to use as the electrolyte layer the separator holding the gel-like material.

[0056]

The polymer material used in the present invention for preparing the gel-like material includes, for example, a monomer or polymer of polyacrylonitrile, polyvinylidene fluoride (PVdF) or polyethylene oxide (PECO), or a copolymer between any of these monomers and another monomer.

[0057]

It is also possible to use as the nonaqueous electrolyte layer a solid polymer electrolyte layer prepared by dissolving an electrolyte in the polymer material, followed by solidifying

the resultant solution. The polymer material used in the present invention for preparing the solid polymer electrolyte layer includes, for example, a monomer or polymer of polyacrylonitrile, polyvinylidene fluoride (PVdF), or polyethylene oxide (PEO), or a copolymer between any of these monomers and another monomer. It is also possible to use an inorganic solid electrolyte for forming the nonaqueous electrolyte layer. The inorganic solid electrolyte used in the present invention includes, for example, a ceramic material containing lithium. To be more specific, the inorganic solid electrolyte noted above includes, for example,  $\text{Li}_3\text{N}$ ,  $\text{Li}_3\text{PO}_4\text{-Li}_2\text{S-SiS}_2$ , and  $\text{LiI-Li}_2\text{S-SiS}_2$  glass.

[0058]

The first nonaqueous electrolyte secondary battery according to the present invention described above comprises a negative electrode containing an alloy having a  $\text{TiNiSi}$  type crystal structure. The alloy of the particular crystal structure does not perform an alloying reaction with lithium when lithium ions are interposed between the adjacent layers of the crystal in the charging stage. Also, the interposed lithium ions are released from between the adjacent layers of the crystal in the discharge stage. It follows that lithium can be intercalated into and deintercalated from between the adjacent layers of the crystal without bringing about the alloying reaction between the alloy and lithium in the charge-discharge stages so as to enhance the reversibility of the intercalation/deintercalation reaction of lithium. It is also possible to increase the stability of the crystal because the

volume expansion can be suppressed in the lithium insertion stage. Further, it is possible to suppress the reaction between the negative electrode and the nonaqueous electrolyte. It follows that the Coulomb efficiency can be increased during the charge-discharge cycle so as to realize high charge-discharge cycle characteristics.

[0059]

It should also be noted that, in the present invention, the lattice constant of the crystal axis  $b$  of the alloy having the TiNiSi type crystal structure is set to fall within a range of  $4\text{\AA}$  to  $5.5\text{\AA}$  so as to carry out smoothly the intercalation/deintercalation reaction of lithium. It follows that the charge-discharge cycle characteristics of the secondary battery can be further improved.

[0060]

The alloy having the TiNiSi type crystal structure has a composition represented by formula (1) given previously. In this case, the alloy density can be increased to a high level, i.e., can be increased to  $7.8\text{ g/cm}^3$  on the average, so as to make it possible to further increase the capacity per unit volume. It follows that it is possible to provide a secondary battery excellent in the capacity per unit volume and in the charge-discharge cycle characteristics.

[0061]

A second nonaqueous electrolyte secondary battery according to an embodiment of the present invention will now be described. The nonaqueous electrolyte secondary battery comprises a positive electrode, a negative electrode containing

an alloy having a ZrBeSi type crystal structure, and a nonaqueous electrolyte layer provided between the positive electrode and the negative electrode. The positive electrode and the nonaqueous electrolyte layer similar to those described previously in conjunction with the first nonaqueous electrolyte secondary battery can be used here. Such being the situation, the negative electrode included in the nonaqueous electrolyte secondary battery according to this embodiment will now be described.

[0062]

FIG. 2 schematically shows the construction of the unit cell of the ZrBeSi type crystal in the case where the alloy has a LaNiSn composition. Specifically, the circles shaded with oblique lines, which are shown in FIG. 2, denote La sites, the white circles denote Ni sites, and the circles shaded with dots denote Sn sites.

[0063]

It is possible for the alloy to be a single phase alloy consisting of a ZrBeSi type crystal phase or to be a polyphase alloy including a ZrBeSi type crystal phase and another crystal phase.

[0064]

The crystal axis "a" of the ZrBeSi type crystal is the crystal axis parallel to the depth direction in FIG. 2. Lithium is interposed between the adjacent layers in a direction perpendicular to the crystal axis "a". It is desirable for the lattice constant of the crystal axis "a" to fall within a range of 4Å to 5.5Å. That is because, if the

lattice constant of the crystal axis "a" is smaller than  $4\text{\AA}$ , the interposition of the lithium ions between the adjacent layers of the crystal tends to be rendered difficult, and on the other hand, if the lattice constant of the crystal axis "a" exceeds  $5.5\text{\AA}$ , it is possible for the ZrBeSi type crystal phase to fail to be obtained. It is more desirable for the lattice constant of the crystal axis "a" to fall within a range of  $4.2\text{\AA}$  to  $5.3\text{\AA}$ .

[0065]

It is possible to prepare an alloy having the ZrBeSi type crystal structure by, for example, an induction heating method. In the induction heating method, it comprises pouring a melt onto a rotating cooling plate in the casting stage. It is possible to control the thickness of the deposited melt by adjusting the melt supply rate and the moving speed of the cooling plate, thereby controlling the cooling rate. A heat treatment is applied to the obtained sample so as to homogenize the texture and the composition of the alloy.

[0066]

The negative electrode can be prepared by a method similar to that described previously in conjunction with the first nonaqueous electrolyte secondary battery.

[0067]

The second nonaqueous electrolyte secondary battery of the present invention described above comprises a negative electrode containing an alloy having a ZrBeSi type crystal structure. The alloy of the particular crystal structure makes it possible to intercalate or deintercalate lithium into or out

of between the adjacent layers of the crystal without bringing about an alloying reaction between the alloy and lithium. As a result, the reversibility of the intercalation/deintercalation of lithium can be enhanced. It is also possible to increase the stability of the crystal because the volume expansion can be suppressed in the lithium insertion stage. Further, it is possible to suppress the reaction between the negative electrode and the nonaqueous electrolyte. It follows that the Coulomb efficiency can be increased during the charge-discharge cycle so as to realize high charge-discharge cycle characteristics.

[0068]

It should also be noted that, the lattice constant of the crystal axis "a" of the alloy having the ZrBeSi type crystal structure is set to fall within a range of 4Å to 5.5Å so as to carry out smoothly the intercalation/deintercalation reaction of lithium. It follows that the charge-discharge cycle characteristics of the secondary battery can be further improved.

[0069]

As described above, the alloy having any of the TiNiSi type crystal structure or the ZrBeSi type crystal structure makes it possible to permit lithium to be intercalated into and deintercalated from between the adjacent layers of the crystal without bringing about the alloying reaction between the alloy and lithium in the charge-discharge stages. It is considered reasonable to understand that the particular function can be achieved as follows.



[0070]

As pointed out in Jpn. Pat. Appln. KOKAI Publication No. 2001-250541 (Patent document 1, paragraph [0009]) referred to previously, different elements M1 and M2 are alternately present on a plane constituting the same layer in the  $\text{Ni}_2\text{In}$  type crystal structure. As a result, the agglomeration of M1 atoms caused by the alloying reaction with lithium is suppressed so as to stabilize the structure. On the other hand, the  $\text{TiNiSi}$  type crystal structure or the  $\text{ZrBeSi}$  type crystal structure of the alloy used in the present invention is featured in that two kinds of atoms other than Ln are alternately bonded with each other so as to form a hexagonal plane such as graphite. In this case, it is considered reasonable to understand that there is an electron orbit that permits electrons to be given to and received from the lithium ion in a direction perpendicular to the formed hexagonal plane. In addition, since the coupling between the adjacent atoms is more stable than that of the  $\text{Ni}_2\text{In}$  type crystal structure, it is possible for the intercalation reaction rather than the alloying reaction to take place.

[0071]

Each of the first and second nonaqueous electrolyte secondary batteries according to the present invention can be applied to batteries of various shapes such as a cylindrical secondary battery, a secondary battery having a rectangular cross section, and a thin plate type secondary battery. FIG. 3 exemplifies the construction of the cylindrical nonaqueous electrolyte secondary battery, and FIG. 4 exemplifies the

construction of the thin plate type nonaqueous electrolyte secondary battery.

[0072]

As shown in FIG. 3, an insulating body 2 is arranged in the bottom portion of a cylindrical case 1 made of, for example, stainless steel and having a bottom. An electrode group 3 is housed in the case 1. The electrode group 3 is prepared by spirally winding a laminate structure comprising a positive electrode 4, a negative electrode 6 and a separator 5 interposed between the positive electrode 4 and the negative electrode 6.

[0073]

A nonaqueous electrolysis solution is housed in the case 1. An insulating paper sheet 7 having a central open portion is arranged above the electrode group 3 within the case 1. An insulating sealing plate 8 is fixed by caulking to the upper open portion of the case 1. A positive electrode terminal 9 is fitted in the center of the insulating sealing plate 8. Further, a positive electrode lead 10 is electrically connected at one end to the positive electrode 4 and to the positive electrode terminal 9 at the other end. On the other hand, the negative electrode 6 is electrically connected to the case 1, which acts as a negative electrode terminal, via a negative electrode lead (not shown).

[0074]

The thin plate type electrode group 11 as shown in FIG. 4 has a structure prepared by spirally winding in a flattened shape a laminate structure including a positive electrode 12,

a negative electrode 13, and a separator 14 interposed between the positive electrode 12 and the negative electrode 13. A band-like positive electrode terminal 15 is electrically connected to the positive electrode 12, and a band-like negative electrode terminal 16 is electrically connected to the negative electrode 13. The electrode group 11 is housed in a case 17 formed of a laminate film such that the edge portions of the positive electrode terminal 15 and the negative electrode terminal 16 protrude from within the case 17. The case 17 formed of a laminate film is sealed by means of a heat seal.

[0075]

Incidentally, the shape of the electrode group housed in the case is not limited to the spiral shape as shown in FIG. 3 or to a flat plate shape as shown in FIG. 4. It is also possible to prepare the electrode group by laminating a positive electrode, a separator and a negative electrode in the order mentioned a plurality of times.

[0076]

[Examples]

Examples of the present invention will now be described in detail with reference to the accompanying drawings.

[0077]

(Examples 1 to 16)

<Preparation of Positive Electrode>

In the first step, prepared was a positive electrode having an electrode density of  $3.0 \text{ g/cm}^3$  by adding 2.5% by weight of an acetylene black, 3% by weight of graphite, 3.5% by

weight of polyvinylidene fluoride (PVdF), and N-methyl pyrrolidone (NMP) to 91% by weight of lithium cobalt oxide ( $\text{LiCoO}_2$ ) powder used as a positive electrode active material while stirring the solution, followed by coating a current collector formed of an aluminum foil having a thickness of 15  $\mu\text{m}$  with the resultant mixture and subsequently drying the coating and, then, pressing the coating.

[0078]

<Preparation of Negative Electrode>

For preparation of a negative electrode active material, prescribed amounts of elements were mixed at the composition ratio shown in Table 1, followed by once casting the mixture in a thickness of about 10 mm on a water-cooled circular template by means of a induction heating and subsequently applying an additional induction heating to the cast mixture so as to obtain a melt. Then, the melt thus obtained was sprayed onto a cooling roll rotated at a speed of 40 m/s so as to obtain a flake-like intermetallic compound layer having a thickness of 10 to 30  $\mu\text{m}$ , thereby obtaining a negative electrode active material.

[0079]

In the next step, a negative electrode was prepared by adding 5% by weight of graphite used as an electrically conductive agent, 3% by weight of an acetylene black that was also used as an electrically conductive agent, 7% by weight of PVdF, and an NMP solution to 85% by weight of the intermetallic compound powder while stirring the solution, followed by coating a current collector formed of a copper foil having

a thickness of 11  $\mu\text{m}$  with the resultant mixture and subsequently drying the coating and, then, pressing the coating.

[0080]

<Preparation of Electrode Group>

An electrode group was prepared by laminating the positive electrode noted above, a separator formed of a polyethylene porous film, the negative electrode noted above, and separator noted above in the order mentioned, followed by spirally winding the laminate structure such that the negative electrode is positioned to form the outermost circumferential surface.

[0081]

<Preparation of Nonaqueous Electrolysis Solution>

Further, a nonaqueous electrolysis solution was prepared by dissolving lithium hexafluoro phosphate ( $\text{LiPF}_6$ ) in a mixed solvent prepared by mixing ethylene carbonate (EC) with methyl ethyl carbonate (MEC) (a mixing ratio by volume of 1 : 2). Lithium hexafluoro phosphate was dissolved in the mixed solvent in an amount of 1 mol/L.

[0082]

Finally, a cylindrical nonaqueous electrolyte secondary battery as shown in FIG. 1 was assembled by housing the electrode group and the nonaqueous electrolysis solution in a cylindrical case made of stainless steel and having a bottom.

[0083]

(Example 17)

A cylindrical nonaqueous electrolyte secondary battery

was assembled as in Example 1, except that an intermetallic compound obtained by mixing prescribed amounts of elements having a composition ratio shown in Table 1, followed by casting the resultant mixture by means of an induction heating method and subsequently applying a heat treatment to the cast body at 900°C for 6 hours under the condition that an inert gas atmosphere was used as the negative electrode active material.

[0084]

The intermetallic compound used in the secondary battery for each of Examples 1 to 17 was analyzed by an X-ray diffraction method. It has been found that the intermetallic compound for each of Examples 1 to 16 contains a TiNiSi type crystal phase, and that the intermetallic compound for Example 17 contains a ZrBeSi type crystal phase. Also, the lattice constant of the crystal axis b of the TiNiSi type crystal and the lattice constant of the crystal axis "a" of the ZrBeSi type crystal were determined from the X-ray diffraction patterns, with the results as shown in Table 1.

[0085]

(Comparative Example 1)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that a Si powder having an average particle diameter of 10  $\mu\text{m}$  was used as the negative electrode active material.

[0086]

(Comparative Example 2)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that a mesophase pitch

based carbon fiber subjected to a heat treatment at 3250°C (an average fiber diameter of 10  $\mu\text{m}$ , an average fiber length of 25  $\mu\text{m}$ , an average layer spacing  $d_{002}$  of 0.3355 nm, and a specific surface area as determined by the BET method of 3  $\text{m}^2/\text{g}$ ) was used as the negative electrode active material.

[0087]

(Comparative Example 3)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that a LiSn alloy was used as the negative electrode active material.

[0088]

(Comparative Example 4)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that an  $\text{FeSn}_2$  alloy having a hexagonal close-packed structure and a  $\text{Ni}_2\text{In}$  type structure was prepared by a roll quenching method and the alloy thus prepared was used as the negative electrode active material.

[0089]

(Comparative Example 5)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that a  $\text{BeSiZr}$  alloy having a hexagonal close-packed structure and a  $\text{Ni}_2\text{In}$  type structure was prepared by a roll quenching method and the alloy thus prepared was used as the negative electrode active material.

[0090]

(Comparative Example 6)

A cylindrical nonaqueous electrolyte secondary battery was prepared as in Example 1, except that a CoSn alloy having

a hexagonal close-packed structure was prepared by a roll quenching method and the alloy thus prepared was used as the negative electrode active material.

[0091]

The secondary battery prepared in each of Examples 1 to 17 and Comparative Examples 1 to 6 was repeatedly subjected to a charge-discharge cycle in which the secondary battery was charged to 4.2V over 2 hours at 20°C under a charging current of 1.5A, followed by discharging the secondary battery to 2.7V under a discharge current of 1.5A at 20°C, so as to measure the discharge capacity per unit volume (mAh/cc) for the first cycle, and the capacity retention rate at the 100<sup>th</sup> cycle (the discharge capacity at the first cycle was set at 100%). Tables 1 and 2 show the results.



[0092]

[Table 1]

[0093]

[Table 2]

[0094]

As apparent from Tables 1 and 2, the discharge capacity per unit volume of the secondary battery for each of Examples 1 to 17 comprising the negative electrode containing an intermetallic compound having a TiNiSi type or ZrBeSi type crystal structure was found to be higher than that for the secondary battery for Comparative Example 2 (carbonaceous material). Also, the capacity retention rate at the 100<sup>th</sup> cycle for the secondary battery for each of Examples 1 to 17 was found to be higher than that for the secondary battery for each of Comparative Examples 1 and 3 to 6.

[0095]

FIG. 5 shows the X-ray diffraction patterns of the negative electrode active material under the initial state (before the charging), the charged state and the discharged state in respect of the secondary battery for Example 5 in which  $(\text{La}_{0.54}\text{Ni}_{0.46})_{44}\text{Sn}_{56}$  intermetallic compound was used as the negative electrode active material. FIG. 5 shows the peaks derived from the TiNiSi type crystal structure. FIG. 5 also shows the X-ray diffraction pattern of the negative electrode active material under the charged state of the secondary battery for Comparative Example 3 in which a LiSn alloy was used as the negative electrode active material. On the other hand, FIG. 6 shows the X-ray diffraction patterns of the negative electrode active material under the initial state (before the charging or before the test), the charged state and the discharged state in respect of the secondary battery for Comparative Example 6 in which a CoSn alloy was used as the

negative electrode active material. FIG. 6 also shows the X-ray diffraction pattern of the negative electrode active material under the charged state of the secondary battery for Comparative Example 3 in which a LiSn alloy was used as the negative electrode active material.

[0096]

As apparent from FIG. 5, the diffraction peak at about  $39.8^{\circ}$  is shifted toward the smaller angle side after the charging in the secondary battery for Example 5, supporting that lithium was intercalated in the charging stage into the intermetallic compound having the TiNiSi type crystal structure. Also, as apparent from the diffraction pattern after the discharge, the shifted diffraction peak was brought back to the original peak position after the discharge. This indicates that the crystal was shrunk while maintaining the skeletal structure of the lattice.

[0097]

On the other hand, the diffraction pattern was not shifted in the secondary battery for Comparative Example 6. However, a peak derived from the alloying reaction between Li and Sn was observed in the vicinity of  $38.3^{\circ}$  in the diffraction pattern after the charging, as shown in FIG. 6. The diffraction peak disappears after the discharge. However, it is known to the art that the generation of the LiSn alloy in the charge-discharge stage brings about a vigorous change in the volume of the alloy active material. It follows that the fine pulverization of the active material causes a deterioration of the charge-discharge cycle.

[0098]

In other words, it is of no difficulty to understand that the intercalation/deintercalation reaction of lithium is reversibly carried out in the secondary battery for Example 5, and that the change in volume of the intermetallic compound accompanying the intercalation/deintercalation reaction of lithium is small.

[0099]

Even if the secondary battery for Example 5 was subjected to 50 charge-discharge cycles, a peak in the vicinity of  $38.3^\circ$  derived from the alloying reaction between Li and Sn was not recognized in the diffraction pattern after discharge for the 50<sup>th</sup> cycle and after the charging in the 51<sup>st</sup> cycle as shown in FIG. 7. On the other hand, a peak in the vicinity of  $38.3^\circ$ , which is derived from the alloying reaction between Li and Sn, was not recognized in the diffraction pattern under the state after the discharge in the tenth cycle of the charge-discharge operation, when it comes to the secondary battery for Comparative Example 6, as apparent from FIG. 8. However, the peak noted above was clearly observed in the diffraction pattern under the state after the discharge in the 50<sup>th</sup> cycle of the charge-discharge operation. The experimental data suggest that the alloying reaction between Li and Sn takes place in the charging stage as in Comparative Example 6 because Li is stored in the alloy as an irreversible capacity by the repetition of the charge-discharge operation, which shortens the charge-discharge cycle life.

[0100]

The present invention is not limited to the above embodiments and can be practiced in various modifications without departing from the spirit and scope thereof. Further, various inventions can be extracted in accordance with proper combinations of a plurality of disclosed components. For example, some components are excluded from the entire components represented in the embodiments. Furthermore, the components covering the embodiments can appropriately be combined with one another.

[0101]

[Advantage of the Invention]

As has been described above in detail, the present invention can provide a nonaqueous electrolyte secondary battery having a large discharge capacity per unit volume and a sufficiently long charge-discharge cycle life.

[Brief Description of the Invention]

[FIG. 1]

A view schematically illustrating the construction of the unit cell of a TiNiSi type crystal.

[FIG. 2]

A view schematically illustrating the construction of the unit cell of a ZrBeSi type crystal.

[FIG. 3]

A cross sectional view schematically showing the construction of a cylindrical nonaqueous electrolyte secondary battery according to one embodiment of the nonaqueous electrolyte secondary battery of the present invention.

[FIG. 4]

An oblique view, partly broken away, schematically showing the construction of a thin plate type nonaqueous electrolyte secondary battery according to another embodiment of the nonaqueous electrolyte secondary battery of the present invention.

[FIG. 5]

A graph showing the X-ray diffraction patterns of the negative electrode active material under the initial state, the charged state and the discharged state in respect of the nonaqueous electrolyte secondary battery for Example 5 and the X-ray diffraction pattern of the negative electrode active material under the charged state in respect of the nonaqueous electrolyte secondary battery for Comparative Example 3.

[FIG. 6]

A graph showing the X-ray diffraction patterns of the negative electrode active material under the initial state (before the test), the charged state and the discharged state in respect of the nonaqueous electrolyte secondary battery for Comparative Example 6 and the X-ray diffraction pattern of the negative electrode active material under the charged state in respect of the nonaqueous electrolyte secondary battery for Comparative Example 3.

[FIG. 7]

A graph showing the X-ray diffraction patterns of the negative electrode active material after the discharge in the 50<sup>th</sup> cycle and after the charging in the 51<sup>st</sup> cycle in respect of the nonaqueous electrolyte secondary battery for Example 5

and the X-ray diffraction pattern of the negative electrode active material under the charged state in respect of the nonaqueous electrolyte secondary battery for Comparative Example 3.

[FIG. 8]

A graph showing the X-ray diffraction patterns of the negative electrode active material after the discharge in the 10<sup>th</sup> cycle and in the 50<sup>th</sup> cycle in respect of the nonaqueous electrolyte secondary battery for Comparative Example 6 and the X-ray diffraction pattern of the negative electrode active material under the charged state in respect of the nonaqueous electrolyte secondary battery for Comparative Example 3.

[Explanation of Reference Symbols]

- 1 ... Case,
- 3 ... Electrode group,
- 4 ... Positive electrode,
- 5 ... Separator,
- 6 ... Negative electrode,
- 8 ... Insulating sealing plate,
- 11 ... Electrode group,
- 12 ... Positive electrode,
- 13 ... Negative electrode,
- 14 ... Separator,
- 15 ... Positive electrode terminal,
- 16 ... Negative electrode terminal,
- 17 ... Case.



Table 1

	Composition of negative electrode active material	Crystal structure	Lattice constant (Å)	Discharge capacity per unit volume (mAh/cc)	Capacity retention rate at 100 <sup>th</sup> cycle (%)
Example 1	(La <sub>0.4</sub> Ni <sub>0.6</sub> ) <sub>40</sub> Sn <sub>60</sub>	TiNiSi type	4.52	1680	84.3
Example 2	(La <sub>0.4</sub> Ni <sub>0.6</sub> ) <sub>80</sub> Sn <sub>20</sub>	TiNiSi type	4.37	985	85.3
Example 3	(La <sub>0.7</sub> Ni <sub>0.3</sub> ) <sub>40</sub> Sn <sub>60</sub>	TiNiSi type	4.94	2012	82.4
Example 4	(La <sub>0.7</sub> Ni <sub>0.3</sub> ) <sub>80</sub> Sn <sub>20</sub>	TiNiSi type	4.78	1822	86.2
Example 5	(La <sub>0.54</sub> Ni <sub>0.46</sub> ) <sub>44</sub> Sn <sub>56</sub>	TiNiSi type	4.73	1869	88.2
Example 6	(Ba <sub>0.4</sub> La <sub>0.2</sub> Ni <sub>0.4</sub> ) <sub>75</sub> Sn <sub>25</sub>	TiNiSi type	5.46	1034	83.1
Example 7	(Nd <sub>0.2</sub> Ce <sub>0.2</sub> Ni <sub>0.6</sub> ) <sub>54</sub> Sn <sub>46</sub>	TiNiSi type	4.62	1794	84.5
Example 8	(Pr <sub>0.1</sub> Y <sub>0.32</sub> Ni <sub>0.58</sub> ) <sub>72</sub> Sn <sub>28</sub>	TiNiSi type	4.41	1012	93.5
Example 9	(Mg <sub>0.53</sub> Ni <sub>0.47</sub> ) <sub>60</sub> Sn <sub>40</sub>	TiNiSi type	4.03	1812	86.6
Example 10	(Pm <sub>0.2</sub> Hf <sub>0.1</sub> Sm <sub>0.1</sub> Ni <sub>0.6</sub> ) <sub>54</sub> Sn <sub>4</sub> 6	TiNiSi type	4.88	1725	85.2
Example 11	(La <sub>0.4</sub> Ba <sub>0.05</sub> Ca <sub>0.05</sub> Ni <sub>0.5</sub> ) <sub>65</sub> S n <sub>35</sub>	TiNiSi type	5.13	1102	92.3
Example 12	(La <sub>0.57</sub> Nb <sub>0.04</sub> Ni <sub>0.39</sub> ) <sub>43</sub> Sn <sub>57</sub>	TiNiSi type	4.88	1821	94.5
Example 13	(La <sub>0.5</sub> Co <sub>0.16</sub> Ni <sub>0.34</sub> ) <sub>44</sub> Sn <sub>56</sub>	TiNiSi type	4.81	1692	96.1
Example 14	(La <sub>0.6</sub> Fe <sub>0.01</sub> Ni <sub>0.39</sub> ) <sub>65</sub> Sn <sub>35</sub>	TiNiSi type	4.52	1103	94.3
Example 15	(La <sub>0.5</sub> Ti <sub>0.2</sub> Ni <sub>0.3</sub> ) <sub>44</sub> Sn <sub>56</sub>	TiNiSi type	4.92	1854	91.3

Example 16	$(\text{La}_{0.52}\text{V}_{0.02}\text{Ti}_{0.06}\text{Ni}_{0.4})_{42}\text{Sn}$ 58	TiNiSi type	4.82	1911	92.5
Example 17	$(\text{La}_{0.5}\text{Ni}_{0.5})_{66.7}\text{Sn}_{33.3}$	ZrBeSi type	4.65	1469.2	95.0

Table 2

	Composition of negative electrode active material	Crystal structure	Discharge capacity per unit volume (mAh/cc)	Capacity retention rate at 100th cycle (%)
Comparative Example 1	Si	-	9800	23
Comparative Example 2	C	-	725.04	97
Comparative Example 3	Li-Sn alloy	-	3254	12
Comparative Example 4	FeSn <sub>2</sub>	Ni <sub>2</sub> In type	1743	32
Comparative Example 5	BeSiZr	Ni <sub>2</sub> In type	1320	54
Comparative Example 6	CoSn	CoSn type	2830	43